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 HARRO TRAUBEL

(54) PROCESS FOR THE PRODUCTION OF POLYURETHANE SHEET

(71) We, BAYER AKTIENGESSELLSCHAFT (formerly known as Farbenfabriken Bayer Aktiengesellschaft), a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement.—

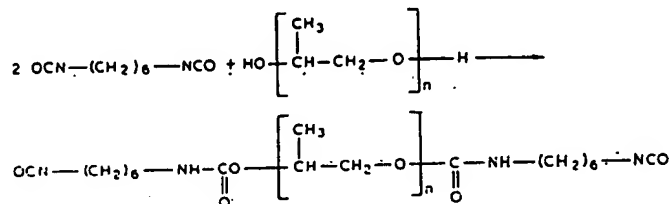
It is known to produce polyurethane sheets, in particular microporous sheets, by a process in which polyurethanes are directly synthesised as sheets, particularly microporous products. Sheets are understood in this context to mean foils, textiles such as fleeces and fabrics laminated with foils, split leather or leather, bonded fleeces and synthetic leather fleeces. One process in which a microporous polyaddition product is synthesised directly by a two-stage process has been found to be especially advantageous. In this process a prepolymer is obtained in known manner from excess polyisocyanate and low molecular weight polyhydroxyl compounds in the first stage. The second reaction stage, the polyaddition of the prepolymer and the chain lengthening agent, is carried out in a reaction medium which dissolves the starting compounds of the polyaddition reaction but in which the polyaddition product is insoluble. The reaction medium is removed during or after the polyaddition. Microporous polyaddition products are obtained directly by this procedure. The procedure is known and has been published e.g. in German Offenlegungsschriften No. 1,694,081 and 1,694,213 and in Belgian Patents No. 715,003; 719,174 and 719,272.

It has been found that carrying out this two-stage reaction on a commercial scale may cause difficulties. If the process is carried out batchwise, the prepolymer has to be kept at elevated temperatures for a prolonged period of time causing viscosity changes and loss of isocyanate groups. It is therefore difficult to obtain uniform polyaddition over prolonged periods of time. Moreover, exact dosing of the prepolymer causes problems owing to its high and inconstant viscosity.

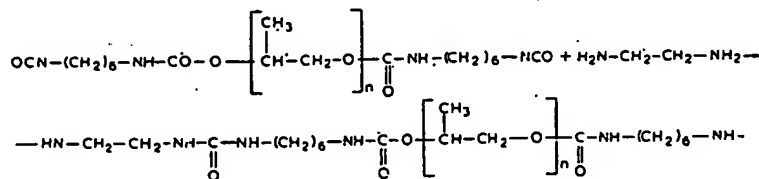
This invention relates to a continuous multi-stage process for the production of a polyurethane sheet in which a compound containing at least two OH groups having a molecular weight of from 600 to 5000 and a polyisocyanate are continuously mixed in a mixing head having a volume of 1 to 1000 cc in quantities corresponding to a molar ratio of NCO groups to OH groups of from 1.3:1 to 7:1 the reactants being delivered continuously into the mixing head from piston dosage pumps and the reaction mixture being discharged from the head by the pressure of the pumps into a reaction vessel of a volume such that the residence time therein results in the prepolymer discharged therefrom having a free NCO group content of from 25% above to 60% below the amount corresponding to complete polyurethane formation, and the prepolymer discharged from the reaction vessel is mixed in a second mixing head with a chain lengthening agent having at least two —OH and/or —NH groups so that the molar ratio of

NCO to active H is from 0.95 to 2 and the mixture is formed into sheets with completion of the polyaddition.

As an example of the process, a polypropylene glycol ether, is reacted with hexamethylene diisocyanate in the first stage to produce a prepolymer as follows:



In the second stage, this prepolymer is reacted with a diamine, e.g. ethylene diamine, to form the high molecular weight, microporous polyurethane polyurea as follows:



Generally starting materials for the process according to the invention are higher molecular weight compounds which contain at least two terminal OH groups, i.e. products having a molecular weight of from 600 to 5000, for example polyethers, polyesters, polycarbonates, polyacetals, polythioethers or polysiloxanes. Such products are known, e.g. from J. H. Saunders and K. C. Frisch "Polyurethanes" I, New York (1962), pages 32 to 61, and from the literature cited there.

Especially to be mentioned are polyesters of adipic acid and dialcohols or mixtures of dialcohols such as ethylene glycol, propylene glycol, butane-1,4-diol, hexane-2,5-diol, 2,2-dimethyl-propane-1,3-diol, hexane-1,6-diol, 2-methylhexane-1,6-diol, 2,2-dimethylhexane-1,3-diol, *p*-bis-hydroxymethyl-cyclohexane, 3-methyl-pentane-1,4-diol or 2,2-diethyl-propane-1,3-diol. Most preferred polyesters are obtained from diols or mixtures of diols which have 5 or more carbon atoms, as they are stable to hydrolysis and yield end products of good elasticity at low temperatures (especially if diols with alkyl side chains are included). Polyesters of caprolactone and diethylene glycol with a narrow range of molecular weights are also suitable, as well as polyesters obtained from diphenylcarbonate and glycols.

Excellently suitable are also polyalkylene ethers such as polypropylene glycols and especially polytetramethylene ether diols; polyalkylene ethers may also be used as mixed polyethers.

The process of the invention can also be carried out with polyhydroxyl compounds which are miscible with water, e.g. polyethylene glycol ether diols, which yield polyurethanes with high water absorption capacity.

The chain lengthening agents, i.e. low molecular weight Zerewitinoff active compounds should have a molecular weight of 18 to 500, preferably 32 to 350. Suitable examples are water and the following compounds, which can be used individually or as mixtures with each other: Ethylene glycol, propylene glycol, butane-1,4-diol, hexane-1,6-diol, hydroquinone-bis-(β -hydroxyethyl ether), *p*-xylene glycol, ethylene diamine, propylene-1,2- or -1,3-diamine, tetramethylene-1,4-diamine, hexamethylene-1,6-diamine, 2,2,4-trimethylhexane-1,6-diamine, 1-methyl-cyclohexane-2,4-diamine, 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane, 4,4'-diamino-dicyclohexylmethane, bis-(aminopropyl)piperazine; aromatic diprimary amines such as 4,4'-diamino-diphenylmethane, bis-2,2-(4-aminophenyl)propane, 4,4'-diamino-diphenylsulphide, 4,4'-diamino-diphenylether, 1-methyl-2,4-diaminobenzene; araliphatic diprimary diamines such as *m*-xylylene diamine, $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-*p*-xylylenediamine, 1,3-bis-(β -amino-isopropyl)-benzene; diamines which contain sulphonic acid groups, e.g. 4,4'-diamino-stilbene-2,2'-disulphonic acid or 4,4'-diamino-diphenylethane-2,2'-disulphonic acid, ethylene diamine-*N*-butylsulphonic acid, hexamethylene-1,6-diamine-*N*-butyl-sulphonic acid, 1,6-diaminohexamethylene-3-sulphonic acid or their alkali metal salts, hydrazides such as carbodihydrazide, oxalic acid dihydrazide, malonic acid dihydrazide, succinic

acid dihydrazide and addition products of ethylene oxide and propylene oxide with ammonia or aliphatic or aromatic amines, e.g. diethanolamine, triethanolamine or methyl diethanolamine or phenyldiethanolamine, which compounds increase the dye ability of the products of the process; also hydrazine, e.g. also in the form of hydrazine hydrate, methylhydrazine and dihydrazines, e.g. N,N'-diaminopiperazine.

Secondary diamines may also be used, preferably those which have a symmetrical structure such as piperazine or 2,5-dimethylpiperazine or 3,3'-dichloro- or 3,3'-dimethyl-4,4'-di(methylaminophenyl)-methane.

Conventional polyisocyanates (described, e.g. by W. Siefken, Liebig's Ann. Chem. 562, 75—136 (1949) or so-called prepolymers which contain at least two NCO groups per molecule, (i.e. prepolymers having an NCO:OH ratio of 1.2 or more) of the above mentioned OH-compounds and excess polyisocyanates are suitable for the process. Suitable polyisocyanates are especially aliphatic, araliphatic, aromatic and heterocyclic diisocyanates or mixtures thereof. Most preferred are diisocyanates of symmetrical structure, e.g. diphenylmethane-4,4'-diisocyanate, diphenyldimethylmethane-4,4'-diisocyanate, 2,2',6,6'-tetramethyl-diphenylmethane-4,4'-diisocyanate, diphenyl-4,4'-diisocyanate, diphenylether-4,4'-diisocyanate or their alkyl substituted, alkoxy substituted or halosubstituted derivatives; tolylene-2,4- and -2,6-diisocyanate and their commercial mixtures, 2,4-diisopropylene-phenylene-1,3-diisocyanate, *m*-xylylene-diisocyanate, *p*-xylylene-diisocyanate and $\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-*p*-xylylenediisocyanate; alkyl substitution products or halosubstitution products of the above mentioned diisocyanates, e.g. 2,5-dichloro-*p*-xylylene diisocyanate or tetrachloro-*p*-phenylenediisocyanate, dimeric tolylene-2,4-diisocyanate, bis-(3-methyl-4-isocyanatophenyl)urea or naphthalene-1,5-diisocyanate. A certain amount of aliphatic diisocyanates such as hexane-1,6-diisocyanate, cyclohexane-1,4-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane or 2,2,4-trimethylhexane-1,6-diisocyanate may also be included and give rise to products which undergo very little discoloration when exposed to light. Diisocyanates such as ω,ω' -di-(isocyanatoethyl)-benzene or 1,2,3,4,5,6-hexahydrodiphenylmethane-4,4'-diisocyanate also result in products which undergo little discoloration on exposure to light.

Best results are obtained with commercially available diphenylmethane-4,4'-diisocyanate, the isomeric tolylene diisocyanates optionally admixed with hexane-1,6-diisocyanate or dicyclohexylmethane-4,4'-diisocyanate.

The preferred chain lengthening agents are aliphatic and aromatic diamines and hydrazine derivatives. Examples are: Hydrazine, methylhydrazine, 4,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylether, 2,4'-tolylenediamine, piperazine, 2,5-dimethylpiperazine and hexamethylenediamine.

If the polyhydroxyl compound has a low molecular weight, e.g. 750 to 1250, the reaction with diisocyanates to form the prepolymers is preferably carried out with low NCO/OH molar ratios, e.g. 2.0:1 to 1.3:1, for polyhydroxyl compounds with a high molecular weight, e.g. 1700 to 2500, high NCO/OH molar ratios are preferably employed, e.g. 3:1 to 1.65:1.

The above mentioned higher molecular weight polyhydroxyl compounds may also be mixed with low molecular weight diols (molecular weight preferably below 250), e.g. ethylene glycol, butane-1,4-diol, bis-N,N-(β -hydroxyethyl)methylamine, bis-N,N-(β -hydroxypropyl)-methylamine, N,N'-bis-hydroxyethylpiperazine or hydroquinone-bis-(β -hydroxyethylether). The quantity of the low molecular weight diols is for example, 10 to 300 mols per cent, preferably 20 to 100 mols per cent, based on the OH groups present. Diols with tertiary nitrogen increase in particular the dyeability, improve the light fastness and provide an active site for subsequent treatments such as cross-linking, for example with strongly alkylating compounds such as 4,4'-dichloromethyl-diphenylether.

The amount of NCO groups present in the prepolymers strongly influences the properties of the polyurethanes produced from them. The NCO content should be at least 0.50% by weight and preferably from 1.00 to 7.6% by weight, and in particular between 1.5 and 4.0% by weight in order that the polyurethane will have sufficiently high melting point, tear resistance, elongation at break and tensile strength. If water is used as chain lengthening agent, the NCO content is preferably from 3.5 to 7.6% by weight because a portion of the NCO groups is then first saponified to amino groups.

The solvents which are preferably used in the process of the invention are organic liquids which boil below 250°C and are inert under the reaction conditions. Suitable solvents are, e.g. aliphatic hydrocarbons such as pentanes, hexanes and homologous cycloalkanes which may be alkylated, such as cyclohexane, methylcyclohexane and cyclododecane.

Mineral oil fractions, especially mixtures of aliphatic hydrocarbons having boiling

points of from 80 to 250°C., e.g. ligroin, cleaning petrol, mineral spirits, turpentine oils, mixed aliphatic-aromatic hydrocarbons such as tetralin or decalin, aromatic hydrocarbons such as benzene, toluene, xylene, ethyl benzene, diethyl benzene or mesitylene, chlorinated hydrocarbons such as di-, tri- and tetrachloromethane, di-, tri- and perchloroethylene, di-, tri-, tetra-, penta- and hexachloroethane, 1,2- and 1,3-dichloropropane, i-butyl chloride, dichlorohexane, chlorocyclohexane, chlorobenzene, chlorotoluene, ethers such as di-n-propyl ether, di-i-propylether, di-n-butyl ether, ethylpropyl ether, anisole or phenetole, esters such as diethyl and dimethyl esters of carbonic acid, ethyl, propyl, butyl, amyl and hexyl esters of acetic acid, methoxybutyl acetate, methylpropionate, ethylpropionate, methyl glycol acetate and dimethyloxalate and ketones such as acetone, methyl ethyl ketone, methyl-i-butyl ketone, methoxyhexanone, mesityl oxide, phorone and cyclohexanone are also suitable solvents.

The reaction of the starting compounds may be catalysed by known isocyanate polyaddition catalysts (see J. H. Saunders and K. C. Frisch "Polyurethanes" I, New York (1962) page 212). It is preferred to use volatile tertiary amines as they practically do not impair the hydrolysis stability of the end products. It is, however, preferred to operate without catalysts in the polyaddition of NCO groups to NH₂ groups.

The following is a preferred way to carry out the process. A solution of the higher molecular weight compound containing at least two hydroxyl groups, e.g. of a polyester, is prepared in a reaction vessel A, the solution of polyisocyanate is prepared in a second vessel B and the solution of chain lengthening agent in the third reaction vessel C. As illustrated in the accompanying drawing, the hot solutions in vessels A and B are now pumped into a mixing vessel M₁, which has a small capacity (approximately 1 to 1000 cm³) but is equipped with a high speed stirrer (approximately 1000 to 10,000 revs/min) by means of the dosing pumps P₁ and P₂, intensively mixed and then conveyed into a reaction vessel G. The size of reaction vessel G is selected to provide a sufficient residence time of the forming prepolymer before its transfer to a second mixing vessel M₂. The solution of chain lengthening agent is also conveyed into the second mixing vessel M₂ by means of a dosing pump P₃ and both solutions are vigorously mixed therein. From mixing vessel M₂ a reacting mixture is discharged which is applied to a substrate. After application on the substrates, i.e. after shaping of the reaction mixture, polyaddition is completed with simultaneous removal of the solvent. If it is desired to produce homogeneous, non-porous sheetings, the solvent is preferably omitted. In that case, the reactants must be liquid at the operating temperature.

The volume of the reaction vessel G used for preparing the prepolymer must be such that at the given rate of feed of polyisocyanate and higher molecular weight polyhydroxyl compound, the prepolymer formed remains in the vessel for a sufficient length of time. This residence time is governed by the reactivity of the isocyanate, the concentration of the prepolymer solution, the polarity of the solvent and the temperature of the solution. The NCO content of the resulting prepolymer on leaving the vessel should be within the limits of 25% above and 60% below the theoretical value, preferably within 15% above and 30% below the theoretical value. If the NCO content is found to be above this limit, this is an indication that unreacted OH groups are still present. Such a prepolymer does not yield a polyurethane with satisfactory properties in a continuous process.

Reference will now be made to certain data, i.e. from Saunders-Frisch "Polyurethanes", Chemistry and Technology, Part 1, New York, 1962 to show the influence of the reaction temperature and of the solvent on the isocyanate-hydroxyl reaction. The reaction of phenyl isocyanate with 1-butanol in xylene is approximately five times more rapid at 35°C than 0°C (page 145). The reaction velocity varies similarly depending on the polarity of the solvent. On page 146 (loc.cit.) it is taught that at 20°C the reaction of phenylisocyanate and alcohol in toluene proceeds 40 times more rapidly than in dioxane.

Furthermore primary hydroxyl groups react approximately three times more rapidly than secondary hydroxyl groups, under identical conditions (see page 145, loc.cit.). The type of isocyanate also influences the velocity of the isocyanate-hydroxyl reaction. Aliphatic isocyanates react approximately 40 times more slowly than aromatic isocyanates.

Concentration of the reactant solutions and the delivery rate of the dosage pumps govern the residence time of the prepolymer in the reaction vessel. Addition of highly polar, high boiling solvents, e.g. N,N-dimethylformamide, N,N-diethylformamide, N,N-dimethylacetamide, N-methyl-morpholine, formylmorpholine, N-acetylmorpholine, N-acetylpyrrolidine, butyrolactone, N,N'-diacetyl piperazine, dimethylsulphone, dipropylsulphone, ethylenecarbonate, methylbenzoate, propiolactone, N-methylpyrrolidone, hexamethylphosphoric acid amine, tetramethyl urea, dimethylsulphoxide, dimethyl-

cyanamide, camphor and mixtures thereof, dimethylformamide and dimethylacetamide being preferred during prepolymer formation, increases the reaction time required; the size of the reaction vessel must then be increased. It is preferred, however, to add these solvents to the chain extending agent and thus control the reaction time of the final chain extending reaction. As a general rule the residence time required in the reaction vessel is 5 to 500 minutes, preferably 15 to 150 minutes. In addition, the spectrum of the residence times should be narrow; this can be achieved most efficiently by using a narrow reaction vessel (height/diameter 2 to 20). This reaction vessel should be equipped with a stirrer which should preferably produce a radial flow without causing mixing in the axial direction.

The process according to the invention may be used for coating substrates. Examples are the coating of textiles, leather, wood, fleeces and concrete, by a direct or reverse process. Furthermore, the products which can be produced by the process of the invention may be used for treating substrates. Examples of this are the bonding of fleeces and the solidification of small particles such as sawdust and wood splinters. The process may, of course, also be coupled, for example substrates may be impregnated and laminated.

The process allows the addition of other polymers; dyes; fillers, stabilisers and cross-linking agents in the form of solutions, organic dispersions or solids; these additional substances are advantageously incorporated in the starting solutions.

One advantage of the process is the wide range of starting materials and solvents which may be used. Products produced by the process may be used as filter materials and as porous coatings for textiles.

Example 1

- 1) 2 kg. of a polypropylene glycol ether (OH number 56) (2 mols of OH) and 2 g. of diaza-bicyclo-octane are heated to 100°C. in a two-litre three-necked flask (product A).
- 2) 1 kg. of a mixture of 65% of 2,4- and 35% of 2,6-tolylene diisocyanate is also heated to 100°C. in a second two-litre three-necked flask (B).
- 3) 500 g. of a liquid mixture of 70% of 2,4- and 30% of 2,6-diamino-3,5-diethyltoluene are heated to 100°C. in a one-litre three-necked flask (product C; see accompanying drawing).

The three flasks were connected to piston-dosage pumps P₁, P₂, P₃.

The delivery rate of the pumps in relation to the piston stroke was determined:

Piston stroke (mm)	P ₁ Quantity of Product A (g/min)	P ₂ Quantity of Product B (g/min)	P ₃ Quantity of Product C (g/min)
0.3	—	—	3.31
0.5	—	5.6	6.62
0.9	—	—	13.2
1.1	—	11.2	—
2.3	—	22.4	—
3.5	26.7	—	—
6.4	53.4	—	—
9	76.9	—	—

The piston stroke of the pump delivering A was adjusted to 3.5 mm (=26.7 g/min) and the piston stroke for B to 0.5 mm (=5.6 g/min) and reactants A+B were delivered through a mixing head M₁ into a reaction vessel G of 700 ml. capacity which was heated with steam at a temperature of 108°C. After leaving the reaction vessel, the prepolymer was delivered into a second mixing head M₂ and mixed with the amine (P₃: 0.3 mm=3.3 g/min) and applied to a steel belt. The resulting film was found to have a tensile strength of 40 kg/cm² and elongation at break of 150%.

Part of the polyurethane sheet was covered with leather and another part with velvetone. The laminate was stripped after 15 minutes. The resulting artificial or semi-artificial leather had good folding strength and solvent resistance.

Part of the reaction solution was used for directly impregnating a fiber fleece and for coating leather. These two experiments were also satisfactory.

Example 2

The following quantities were weighed into three ten-litre three-necked flasks A, B, C:

- 5 A: 1.65 kg. of 4,4'-diisocyanatodiphenylmethane and 6.81 kg. of chlorobenzene;
 B: 6.75 kg. of polyethylene adipate (OH number 56) which had been de-
 hydrated in vacuo ($<0.01\%$ H_2O) and
 1.71 kg. of chlorobenzene;
 10 C: 0.43 kg. of dimethylformamide,
 6.52 kg. of xylene
 0.284 kg. of 4,4'-diaminodiphenylmethane.

All three solutions were heated to $100^\circ C$. with stirring, and connected to piston dosage pumps P_1 , P_2 , P_3 . The rate of feed of individual pumps was then tested at different piston strokes. The following results were obtained.

		P_1	P_2	P_3
	Piston	Quantity of	Quantity of	Quantity of
	stroke (mm)	Product A	Product B	Product C
		(g/min)	(g/min)	(g/min)
15	12	104.6	113.4	153.5
	9	66.9	82.4	110
20	6	52.7	55.9	69.9
	3	24.4	26.8	34.6

In a graph in which the stroke (mm) was plotted along the abscissa against the delivery rate of products A, B or C along the ordinate, straight lines were obtained by connecting the coordinate points. Component A was then delivered to a mixing head M_1 at a piston stroke of 4.8 mm (corresponding to 40 g/Min. of product) and simultaneously component B at a piston stroke of 4.4 mm (corresponding to 51 g/Min.), the mixing head comprising a 34 mm joint equipped with two rubber connections, a 24 mm core with outflow and a stirrer, and from the mixing head into a reaction vessel G equipped with jacket heating and stirrer, which vessel was at a temperature of $96^\circ C$. The prepolymer left the reaction vessel after 70 minutes. It had an NCO content of 1.71% (calculated 1.64% NCO) and was discharged from the vessel at the rate of 79 g/min. At that moment, the third component C was delivered into a second mixing head M_2 at a piston stroke of 6.2 mm (corresponding to 75 g/min) together with the prepolymer. The second mixing head was similar to the first mixing head. The mixed product was delivered to a glass plate, heated to 50 to $60^\circ C$., and dried. After completion of the polyaddition and evaporation of the solvent, a microporous foil having the following physical properties was obtained:

Flexometer: $>200,000$ bends in the Bally Flexometer without damage

Tensile strength: 88 kg/cm²

Elongation at break: 560%

Tear propagation resistance: 12.6 kg/cm at a permeability to water vapor of 11 mg/h.cm².

Equally good results were obtained with experiments carried out similarly on steel plates, teflonised glass fibre fabric (Teflon is a Registered Trade Mark) and separating paper.

Good results were obtained too, if the product according to example 1 was laminated with textile or leather, immediately after being delivered by mixing head M_2 .

WHAT WE CLAIM IS:—

1. A continuous multi-stage process for the production of a polyurethane sheet in which a compound with a molecular weight of from 600 to 5000 and containing at least two-OH groups is mixed with a polyisocyanate in a mixing head having a volume of 1 to 1000 cubic centimetres in quantities corresponding to an NCO/OH molar ratio of from 1.3:1 to 7:1, the reactants being delivered continuously into the mixing head from piston dosage pumps and the reaction mixture being discharged from the head by the pressure of the pumps into a reaction vessel of a volume such that the residence time therein results in the prepolymer discharged herefrom having a free NCO group content of from 25% above to 60% below the amount corresponding to complete polyurethane formation and the prepolymer discharge from the reaction vessel is mixed in a second mixing head with a chain lengthening agent having at least two-OH and/or —NH groups so that the molar ratio of NCO to active H is from 0.95 to 2 and the mixture is formed into sheets with completion of the polyaddition.

2. A process as claimed in claim 1, in which the first and/or second step of the process is carried out in solution in an organic solvent which is inert under the reaction conditions.
3. A process as claimed in claim 2, in which the solvent has a boiling point below 250°C.
4. A process as claimed in claim 3, in which the solvent is an aliphatic or cycloaliphatic hydrocarbon.
5. A process as claimed in any of claim 1 to 4, in which after the addition of the chain lengthening agent, poly-addition is completed by heating.
6. A process as claimed in any of claims 1 to 5, in which the high molecular weight compound is a polyether, polyester, polycarbonate, polyacetal, polythioether or polysiloxane or a mixture thereof.
7. A process as claimed in any of claims 1 to 6, in which the chain lengthening agent has a molecular weight of from 18 to 500.
8. A process as claimed in claim 7 in which the chain lengthening agent has a molecular weight of from 32 to 350.
9. A process as claimed in any of claims 1 to 5, in which the chain lengthening agent is a diprimary aliphatic or aromatic diamine, hydrazine or a substituted hydrazine.
10. A process as claimed in any of claims 1 to 9, in which the polyhydroxyl compound has a molecular weight of from 750 to 1250 and the NCO/OH ratio is from 1.3:1 to 2.0:1.
11. A process as claimed in any of claims 1 to 9 in which the polyhydroxyl compound has a molecular weight of from 1700 to 2500 and the NCO/OH ratio is from 1.65:1 to 3:1.
12. A process as claimed in any of claims 1 to 11 in which the prepolymer is derived from low molecular weight diols in addition to the high molecular weight polyhydroxyl compound.
13. A process as claimed in any of claims 1 to 12, in which the prepolymer has an NCO content of from 1 to 7.6% by weight.
14. A process as claimed in any of claims 1 to 13 in which the prepolymer has an NCO content of from 1.5 to 4.0%.
15. A process as claimed in any of claims 1 to 7 and 10 to 12 in which the chain lengthening agent is water and the NCO content of the prepolymer is from 3.5 to 7.6% by weight.
16. A process as claimed in claim 1 substantially as herein described with reference to any one of the Examples.
17. A process as claimed in claim 1 substantially as herein described with reference to the accompanying drawing.
18. A process as claimed in any of claims 1 to 17, in which other polymers, dyes, fillers stabilisers and/or cross linking agents are added to the reaction mixtures.
19. A polyurethane sheet when produced by a process as claimed in any of claims 1 to 18.
20. A sheet as claimed in claim 19 which is microporous.
21. Textiles, leather, wood, fleeces or concrete when coated with a microporous coating produced by a process as claimed in any of claims 1 to 18.

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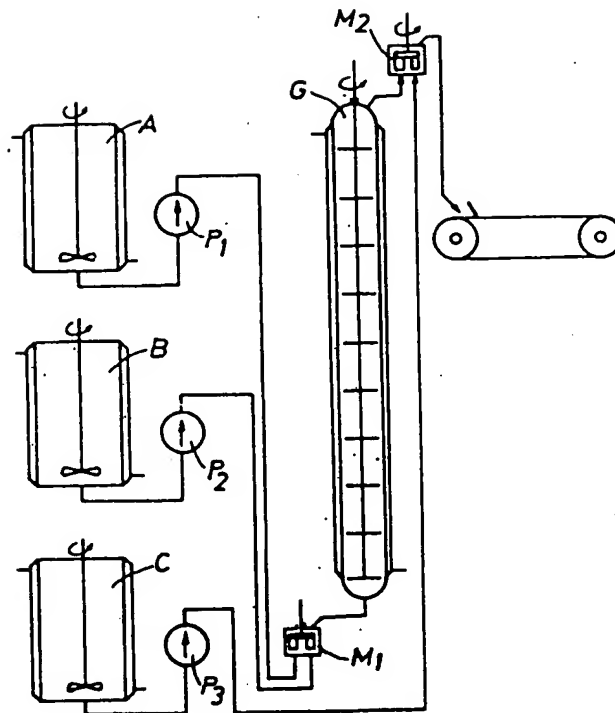
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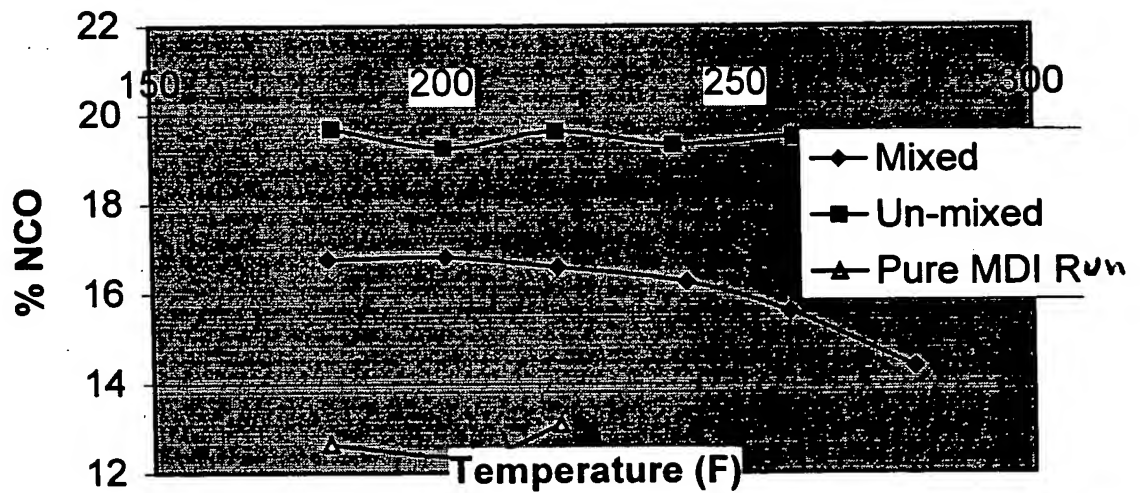
COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*



Effects of mixing tube in continuous Process



"
6" static mixing tube
lower temperature